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Permalink
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Publication Date
1981

Peer reviewed

STRUCTURE AND MELTING OF CD_4 MONOLAYERS ON GRAPHITE[*]

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ABSTRACT

Neutron diffraction studies of monolayer and submonolayer films of CD_4 on graphite have been carried out at two converges $\rho = 1.09$ and $\rho = 0.92$) to investigate the behavior of the structure factor in the two-dimensional solid and across the solid-liquid transition. Detailed lineshape analyses have been carried out. It is found that in the solid phase a characteristic low $-$ K "tail" is seen in the diffraction peak which can be fitted quite well with a power law divergence as expected from scattering by acoustic phonons in a two-dimensional crystal. In the liquid phase, a Lorentzian structure factor accounts reasonably well for the observed lineshape and yields a correlation length that increases rapidly as the solidification temperature is approached. The results are qualitatively in agreement with the predictions of the Kosterlitz-Thouless theory of melting.

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Monolayer and submonolayer films of atoms or molecules physisorbed on solid surfaces provide some fascinating examples of physics in two dimensions (sometimes modified by three-dimensional effects). Because the interaction between the substrate and adsorbate molecules is relatively weak (being typically of the order of $10°K-100°K$), the dominant effects are due to interactions between the adsorbate molecules in the monolayer which results in the occurrence of two-dimensional solid, liquid or vapor phases depending on coverage and temperature. The additional weak "external" periodic potential in the plane due to the crystalline substrate imposes a further complexity into the nature of the phase diagram, since at certain temperatures and coverages it can also cause the adsorbate molecules to "register" into an epitaxial phase commensurate with the substrate. This leads to a variety of interesting two-dimensional phase transitions which can be studied in such sustem, such as the solid-liquid transition or the commensurate-incommensurate transition. Currently, there is a sub-stantial amount of theoretical and experimental work using several techniques, being carried out on such systems.[1]

The most commonly used probe for surface structure is Low Energy Electron Diffraction (LEED), which however requires considerable computational efforts for a detailed quantitative interpretation of the spectra. Neutrons and x-ray diffraction techniques, for which the Born Approximation seems to be valid, and which thus in principle provide a fairly direct measurement of the structure factor of the studied system, are not however primarily surface-sensitive probes. Nevertheless, by making use of graphite substrates in the form of exfoliated graphite which possesses a very large specific surface area (typically 20 m^2 - 60 m^2 per gram), such diffraction techniques have in recent years provided rather detailed structural information.[1-6] Ever since the pioneering adsorption isotherm measurements of Thomy and Duval[7] using rare gas atoms adsorbed on this kind of substrate, it has been known that this substrate presents a fairly homogeneous surface for adsorption [in the sense that the surface area is predominantly made up of (0001) crystallographic planes of graphite], and that fairly sharp phase transitions do occur in the adsorbed layer. The forms of exfoliated graphite most commonly used as substrates for neutron and x-ray diffraction studies are "grafoil" and "ZYX" graphite, which consist of crystallites randomly oriented in the basal planes, but with a partial orientation of the c-axes along the direction normal to the plane of the sample. The former has a fairly large specific surface area ($\sim$ 25 m^2/gm) but a fairly wide angular distribution of the c-axes (corresponding to $\sim$ 30° full width at half maximum) about a common direction, as well as a fairly sizeable misoriented crystallite fraction. The latter has a specific surface area roughly an order

of magnitude smaller but is much more highly oriented, the mosaic spread being $\sim 15°$ full width at half maximum. In grafoil the mean dimension of the crystallites in the basal plane is ~ 400 Å, while in ZYX graphite it is larger by a factor of 2-3.

Graphite is not the only form of substrate used for diffraction investigations of physisorbed systems, however. More recently, other interesting substrates have been investigated, including the lamellar halides[8] and MgO.[9]

We have carried out neutron diffraction studies of monolayer and submonolayer films of CD_4 adsorbed on both grafoil and ZYX graphite. CD_4 was chosen because methane is the simplest hydrocarbon that can be studied in this manner, and except possibly at the lowest temperatures is freely rotating, thus constituting a fairly simple "spherical" molecule of size somewhat greater than Kr, Ar, H_2 and He which had been studied previously.(The deuterated molecule is used to take advantage of the large coherent neutron scattering cross-section which results.) As we shall see, the increased size of CD_4 relative to the previously studied systems does give rise to a more complex phase diagram, which was studied earlier in some detail. Since this work has recently been reported,[6] we shall simply summarize here the main features.

The diffraction studies are carried out by obtaining a difference pattern between the scattering from the grafoil loaded with CD_4 and the empty grafoil as a function of scattering angle. Since CD_4, in common with most of these systems, orders in a close-packed triangular lattice, the first and most prominent diffraction peak due to the monolayer is the (10) peak which fortunately occurs in a region free of any diffraction peaks due to the graphite itself. (Special care had to be taken in filtering the incident neutron beam to remove third-order contamination which can result in a large third-order reflection from the graphite (1120) planes at the same position). The (20) peak from the CD_4 monolayer is unfortunately unobservably small in intensity owing to the destructive interference between the scattering from the C nucleus and the outer D_4 shell in the "form factor", in the case where the molecules are freely rotating. The initial analysis was carried out by fitting to the observed (10) peak a line-shape of the type calculated by Warren [10] for diffraction from a random array of two-dimensional crystallites, and modified[2] for partial orientation effects. This gives a characteristic asymmetric or sawtooth line-shape with some broadening of the leading edge due to finite crystallite size and instrumental resolution effects. We shall return to the question of the detailed line-shape later in this article. At present it suffices to say that one obtains from such a fit the d-spacing of the 2-D crystallite "lines", the size of the 2-D crystallite L, and the intensity parameter I.

These were studied as a function of coverage and temperature and the results obtained are shown in Fig.1. From the d-spacing one notices immediately that the solid exists in both "registered" or epitaxial $\sqrt{3} \times \sqrt{3}$ phase and incommensurate phases which can be expanded or compressed relative to the $\sqrt{3} \times \sqrt{3}$ phase depending on coverage and temperature. (The $\sqrt{3} \times \sqrt{3}$ phase is the most common registered phase seen in such systems, corresponding to adsorption at the centers of rings of graphite atoms with nearest neighbor sites excluded. The nearest neighbor distance is thus $\sqrt{3}$ times the C-C distance in the graphite plane). Coexisting solid-vapor phases can be identified by a rapid and roughly linear decrease in both the intensity of scattering from, and size of the crystallites with increasing temperature. Liquid phases can be identified by the appearance of a very broad and weak diffraction maximum instead of the sharper solid-like peak. The transition between solid and liquid-like behavior for the diffraction peak appears to be rather sudden as a function of temperature at high coverages. At fixed coverage, then, this would indicate a second-order phase transition. At lower coverages, co-existing solid and liquid phases appear to exist, indicating a first-order melting process. The phase diagram deduced from these earlier measurements is shown in fig.2. We have not explicitly differentiated between liquid and gas phases in these results, since diffraction measurements alone are unable to determine such a difference, but at low coverages. "Fluids" must correspond to a vapor-like phase and at higher coverage to a liquid-like phase. The commensurate-incommensurate transition as a function of coverage and temperature has also been studied in this system[6] (and also more recently in CD_4 on ZYX graphite in collaboration with M. Nielsen - to be published), but we shall not discuss those aspects in the present paper.

Further experiments were carried out at the HFBR Reactor at Brookhaven National Laboratory to study the melting process in more detail. In three dimensions, as is well known, melting is a strongly first-order transition, and the microscopic details of the process are not completely clear. On the other hand, in two dimensions there are theoretical grounds for believing that melting can be a continuous process under certain circumstances, and in fact Kosterlit and Thouless [11] have provided a microscopic description of the melting process in terms of a catastrophic unbinding of dislocation-pairs. Their work was extended more recently by Halperin and Nelson[12] using renormalization group theory. They showed that the 2D melting process in fact proceeds through an intermediate phase in which positional correlations become short range but where long range orientational order of the bonds between atoms is preserved (termed the "hexatic" phase, in the case of a triangular lattice) and then at a slightly higher temperature, to an isotropic 2D fluid. In addition, there is the related and interesting question of the absence of true long range order in a
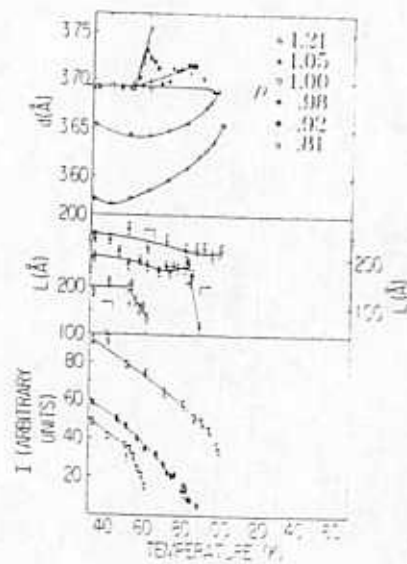
Fig.1 :

Plots of lattice plane spacing d, cluster size L and peak intensity I vs. temperature for various coverages. The arrows denote a change in phase as indicated by Fg.2.
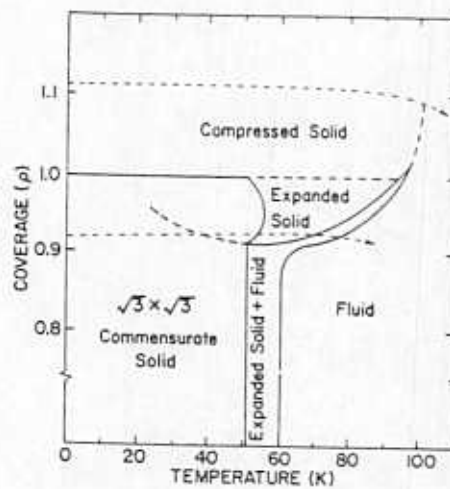

Fig.2 :

Phase diagram for CD₄ on graphite. The dashed curves present coverages at which further detailed melting measurements were taken

2D crystal. It was shown many years ago by Peierls[13] and later
by Mermin and Wagner[14] that long range order could not exist in
the sense that the mean-square displacement due to phonon
fluctuations diverges logarithmically with the crystal size.
It has been shown[15,16] that for an infinite harmonic 2D crystal
this implies a power-law divergence of the structure factor at the
reciprocal lattice points instead of the usual delta functions
corresponding to "Bragg Peaks" in the 3D case. All of the above
considerations strictly speaking apply to infinite 2D crystals on
smooth substrates. A solid phase of the monolayer which is
incommensurate with the substrate may roughly be expected to
approximate this situation at reasonably high temperatures,
although the detailed effect of the substrate periodicity has not
yet been rigorously treated theoretically. We shall discuss finite
crystalline size effects later.

One of the interesting aspects of the Kosterlitz-Thouless
transition is that it has no signature in the specific heat, being
of the nature of an essential singularity. However, from the point
of view of diffraction experiments, it does have a signature which
is principle observable. This is due to the fact that the
correlation length in the fluid phase is predicted to diverge
continuously with decreasing temperature as the solid phase is
approached, thus sharply differentiating it from the freezing
transition in three dimensions. Specifically, the theory of
Halperin and Nelson[12] yields the results that in the "hexatic"
fluid phase, the structure factor is given by

$$S(\vec{K}) = \frac{2}{G} \tilde{S}_G (\vec{K} - \vec{G}) \tag{1}$$

where $\vec{K}$ is the wave vector transfer and $\vec{G}$ is a reciprocal lattice
point (which is still meaningful here since orientational order
is preserved), and $\tilde{S}_G(\vec{q})$ is approximately given by

$$\tilde{S}_G(\vec{q}) = \frac{\xi^{2 - \eta_G^*}}{(q^2 \xi^2 + 1)^{1 - \frac{1}{2} \eta_G^*}} \tag{2}$$

where ξ is the correlation length, and η_G^* is a constant which
cannot be larger than 1/3 and is calculated to be 1/4 for the
case considered by Halperin and Nelson[12]. As $\xi \to \infty$ it may be
seen that $S_G(\vec{q})$ goes over to the power-law-divergent structure
factor for the infinite 2D crystal. The temperature dependence
of ξ is given by :

$$\xi = \xi_0 \exp [A(T-T_0)^{-\nu}) \tag{3}$$

where ν is calculated by Halperin and Nelson to be 0.369 ... and T_0 is the transition temperature. Below T_0, $\tilde{S}_G(\vec{q})$ has been calculated(16) to be of the form

$$\tilde{S}_G(\vec{q}) \simeq A \frac{\eta}{4} \left(\frac{2}{qa}\right)^{2-\eta}$$

(4)

where A is a constant and a is the lattice constant. Equation (4) represents the Fourier transform of a real-space correlation function that decays as $r^{-\eta}$ and is rigorously valid for small η only. On the other hand, the assumptions on which the Warren line-shape theory is based (namely a perfectly ordered lattice but of finite size L) yield

$$\tilde{S}_G(\vec{q}) = AL^2 \exp\left(-\frac{q^2 L^2}{4\pi}\right)$$

(5)

In order to test these various models, we must have a method of deriving the line shape of a diffraction peak for an arbitrary form of $S_G(\vec{q})$. [We assume that for a particular crystallite in the vicinity of a particular reciprocal lattice point, only the corresponding $S_G(\vec{q})$ contributes appreciably to $S(\vec{k})$]. This is accomplished by projecting the scattering from a particular 2D reciprocal lattice "rod" (note that the scattering is independent of the component of scattering wave vector normal to the crystallite plane) onto the scattering plane, making a suitable average of the distributions of the normals to the various crystallite planes, folding with the instrumental resolution and averaging over a random orientation of crystallites in the scattering plane. The observed intensity for a set scattering wave vector $\vec{K}$ in the scattering plane is then given by

$$I(K) = \int_0^\infty dK'K' \, \overline{S}(K') \, F(K,K')$$

(6)

where

$$F(K,K') = \int dK'' \frac{R(K-K'')}{(K'')^2} \frac{\Delta(K'-K'')}{[1 - (\frac{K'}{K''})^2]^{1/2}}$$

$$\int_\beta^{\pi-\beta} d\theta \frac{p(\theta)}{[(\frac{K'}{K''})^2 - \cos^2\theta]^{1/2}}$$

(7)

$$\overline{S}(K') = f^2(K') \int_0^{2\pi} d\psi \, S_G[(K'^2 + G^2 - 2K'G \cos \psi)^{1/2}] \qquad (8)$$

In Eq.(7), $R(\Delta K)$ is the instrumental resolution function;

$\Delta(x) = 0$ for $x > 0$ and $= 1$ for $x \leqslant 0$; $\beta = \sin^{-1}[1 - (\frac{K'}{K''})^2]^{1/2}$

and $P(\theta)$ is the distribution of crystallites whose normals make an angle θ with the normal to the scattering plane. In Eq.(8), $f(K')$ is the molecular "form factor" for freely rotating CD_4.

The measurements were made at coverages of $\rho = 1.09$ and $\rho = 0.92$ ($\rho = 1.0$ corresponds to the completed registered monolayer coverage - see Fig.2). At $\rho = 1.09$, the monolayer is in the dense incommensurate phase and appears to melt continuously at a temperature of ~ 97 K. At $\rho = 0.92$, the monolayer is in the $\sqrt{3} \times \sqrt{3}$ registered phase below 50 K, then goes into an expanded incommensurate solid phase until a temperature of 60 K is reached. Between 60 K and 70 K, a solid-liquid coexistence region is observed, and above 70 K it is in the fluid phase. Although nominally the coverage is maintained constant, an increase of vapor pressure as the temperature is increased produces a slight decrease in the actual coverage so that the trajectories followed are actually as shown in Fig.2.

We first discuss the measurements made on the incommensurate solid phases. Using Eqs.(6-8), numerical least squares fits to the observed line-shape were made using the "power-law" structure factor given in Eq. (4) and the Gaussian or "Warren" structure factor given in Eq. (5). A typical lineshape for the solid CD_4 (10) peak is shown in Fig. 3(a). Note the characteristic "tail" on the low angle (or small K) side of the main peak. It is clear that the Warren lineshape is unable to fit this tail whereas the power-law is. Thus it seems reasonable to assume that this tail arises from the phonon fluctuations ("thermal diffuse scattering") on which the derivation of Eq. (4) is based. The question of the presence or absence of long range order is moot here, since for finite crystallites there will always be a "Bragg" peak of width $\sim \frac{1}{L}$ in q-space (because there is a small-q cut off for the acoustic phonon spectrum) while for $q \gg \frac{1}{L}$, Eq.(4) should still hold,[16] and corresponds to the thermal diffuse scattering contribution. Thus pattern η are not to be taken seriously. Nevertheless, the following qualitative observations can be made : At $\rho = 1.09$, η stays fairly small and suddenly increases for $T > 95$ K just below the melting temperature. At $\rho = 0.92$, in the
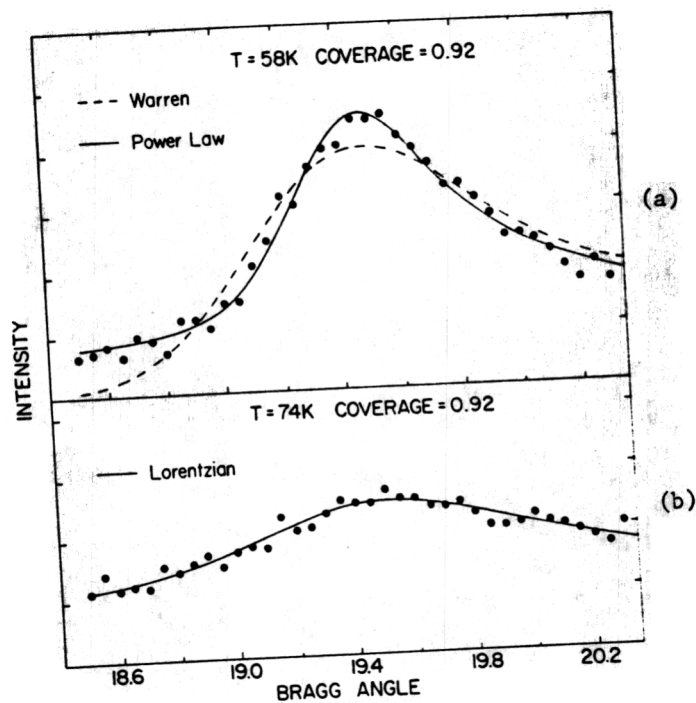
Fig.3(a) :

A typical lineshape for the solid CD_4 (10) peak.
Curves present fits using the Warren lineshape (dashed) and the power law (solid).

Fig.3(b) :

A typical lineshape for the fluid peak.
The solid line presents a fit using the Lorentzian structure factor lineshape.

pure expanded solid phase, η is considerably larger (which is reasonable since the density is lower) and increases with temperature. Above 60 K the fit is not meaningful owing to the solid-liquid coexistence. Interestingly, below 50 K in the commensurate phase, a low-K "tail" was also observed although it was weaker than in the incommensurate phase. This implies that the "gap" induced in the acoustic phonon spectrum by locking to the substrate periodicity is rather small. A detailed theoretical analysis of the structure-factor including phonon fluctuations for this case has been performed recently by Landman.(17)

We now discuss the measurements in the liquid phase above the melting temperature. For this purpose, Eq. (2) was used with $\tilde{S}_G(\vec{q})$ approximated by a Lorentzian structure factor corresponding to setting $1 - \frac{1}{2}\eta_G^* \simeq 1$ in the exponent). Figure 3(b) shows a typical lineshape fitted in this manner. The amplitude of the Lorentzian and ξ were taken as the fitting parameters. Figure 4(a) and (b) show the behavior of ξ as a function of temperature for the two coverages. It can be seen that at high temperature, the correlation length is fairly constant at $\sim$ 30 Å (note that this is already much larger than correlation lengths in 3D liquids) and then rapidly begins to increase as the temperature is decreased. However, instead of diverging, ξ saturates due to finite size effects as the temperature is lowered. (At $\rho = 0.92$, as noted, the first-order transition at 70 K in any case preempts the divergence of ξ to infinity). Thus it is difficult to determine the true transition temperature for the critical behavior. For $\rho = 1.09$, it can be placed within the limits of 96 K and 98 K, inside which region the power-law "solid" and Lorentzian "fluid" lineshape fits have been overlapped. Figure 4(a) and (b) also show a fit of the Halperin-Nelson theory for the temperature dependence of ξ [Eq.(3)], using ξ_o and T_o as fitting parameters, for the two coverages. Also shown is a fit to a straight power law divergence of the form $A[T-T_o]^{-\nu}$. Only points which are clearly in the fluid phase have been used for these fits, since ξ would presumably be affected close to the solidification temperature by finite size effects in a manner that has not as yet been theoretically analyzed. It may be seen that owing to the relatively small number of points, it is not really possible to distinguish between the models and to demonstrate the validity of Eq. (3). Figure 5 shows a plot of ln I vs. ln ξ, where I is the amplitude of the Lorentzian. In both cases a reasonable straight line is observed with a slope slightly less than 2 as predicted by the theory [see Eq. (2)]. Also shown are points corresponding to temperatures clearly in the solid (for $\rho = 1.09$ or coexisting solid/fluid (for $\rho = 0.92$) phases, for which the Lorentzian structure factor is presumably not valid. In each case, a
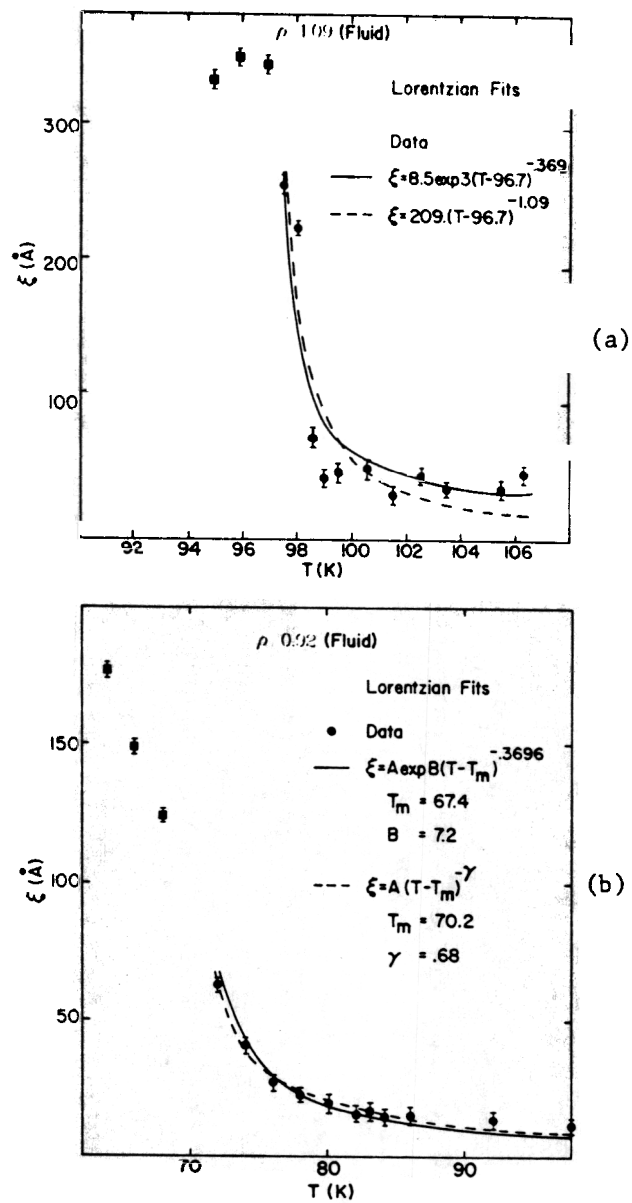
Fig.4 :

Temperature dependence for the correlation length (ξ).
For the fluid phase, the curves present fits using the Ha
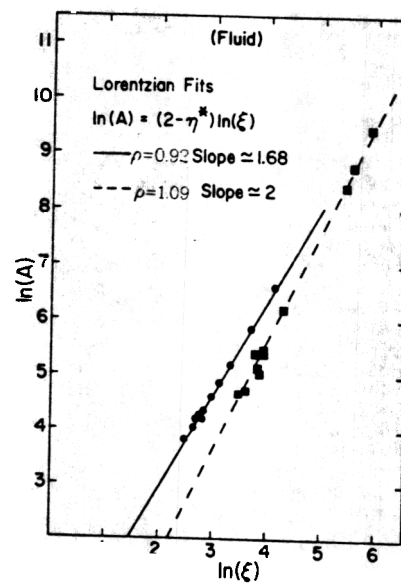Nelson theory (solid) and a straight power law (dashed)

Fig.5 :

A plot of ln(I) vs. ln(ξ) for two representative coverages.
A straight line is observed as predicted by theory.

departure of the plot from linearity is observed which also helps to identify the position of the transition.

In conclusion, the present measurements and associate ine-shape analyses demonstrate :

(a) that in the 2D solid phase, thermal diffuse scattering corresponding to phonon fluctuations is observable and can be fitted by a power law structure factor, although a more detailed analysis including finite size effects is required;

(b) the line-shapes in the 2D liquid phase are approximately consistent with the predictions of the Halperin-Nelson theory and show a tendency for ξ to diverge near the solidification temperature, but do not rule out other forms of this divergence such as a simple power law.

Clearly further work has to be done in incorporating finite size effects into the theory and the lineshape itself. Finally, the effects of second layer promotion [which clearly exists to some extent at $\rho = 1.09$[6]], substrate potential and possible impurities in the monolayer on the observed transition are still unknown.

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